ROLE OF THE TEMPERATURE FACTOR DURING THE WEATHERING OF MINERALS

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One of the main factors which determines the direction and /133* rate of chemical processes is the temperature. Processes of powerful crust formation and the accumulation of many minerals are related to increased temperatures. However, the absence of precise data on the mechanism of chemical reactions occurring during the weathering of minerals makes it impossible to use computational methods to make a quantitative estimate of the role of the temperature factor. In this connection, the Laboratory of Supergene Processes of the Institute of Geology of Ore Deposits, Pletrography, Mineralogy, and Geochemistry of the USSR Academy of Sciences performed the present research. The purpose was to experimentally determine the influence of temperature upon the quantitative decomposition of minerals by natural weathering agents.

The study was performed with a sample of the decomposition of biotite and nepheline at atmospheric pressures at temperatures from $+5^{\circ}$ C to $+70^{\circ}$ C. Following were the reagents: distilled water; water soluble humic acid (i.e., fulvic acid and an ulmic fraction of humic acids) separated from the humus-illuvial layer (Bh) of the podzol of the Karel' isthmus; oxalic acid, which is present in sol solutions in the greatest amounts, and sulfuric acid for comparison. The acid concentration (0.005 N) was determined by potentiometric titration up to pH = 7.0. The experiments lasted for a few days, T: i = 1: 100.

^{*}Numbers in the margin indicate pagination of original foreign text.

Different results were obtained for biotite and nephelene; therefore, it is best to consider them individually.

Decomposition of biotite. The results given in Table 1 show that, with a change in temperature from $+5^{\circ}$ C to $+70^{\circ}$ C, the total decomposition of biotite increases under the action of sulfuric and fulvic acids by approximately a factor of 2.5; by ulmic acid — 3; by oxalic acid — 3.4; and under the influence of water — 2.5 (from $+5^{\circ}$ to $+60^{\circ}$ C). In the range of tempera- /135 tures studied, the dependence of the total decomposition of biotite on temperature is close to rectilinear. This makes it possible to establish its influence on decomposition: thus, an increase in temperature by each 10° causes an increase in the total biotite decomposition for water by 1 mg/l (or by 0.1%); for humic acids and H_2SO_4 — by approximately 10 mg/l (or by 0.1%); and for $H_2C_2O_4$ — by approximately 15 mg/l (or by 0.15%).

Under the experimental conditions, the acids studied changed all the components of biotite into solution, but in different ratios than in the original mineral, whereas water only the alkali elements, magnesium, and silicic acid. In the general case, an increase in temperature had the greatest influence on the behavior of silicic acid. Thus, if the amount of alkalis, which change into solutions of acids from +5° to +70° C, increases by approximately a factor of two, the amount of silicic acid increases by 3 - 3.2 (solutions of H₂SO₄, ulmic acid and fulvic acid), by a factor of 4.3 in solutions of oxalic acid, and by a factor of 10 in aqueous solutions. The percent of the element in the solution with respect to the initial content in the mineral and the ratio SiO2:AI2O3 in the solutions indicate that, with a temperature increase, the amount of silicic acid increases in the solutions. This fully coincides with the characteristics of the biotite structure and the energy of individual bonds.

TABLE 1*

INFLUENCE OF TEMPERATURE ON TOTAL DECOMPOSITION OF BIOTITE (mg/1 in %)

emper ature	0.005 and oxalic acid pH in mg//; sto_nip;	(pH of podzol layer) pH in. mg/l suc way p pH fin. in solution p	·(pH podzol layer)	0.005 and H ₂ SO ₄ off in mg/l ⁵¹⁰ 2, 122 off fin in solution in	oH in. mg/1 ≯
5°C	2,65 2,78 49,17 0,49 1,31	3,07 37,82 0,38 1,68 3,25	2,80 35,24 0,35 1,28 2,97	2,50 48,97 0,49 1,50 2,46	5,97 4,00 0,04 6,80
20° 00	2,62 2,64 52,62 0,53 I,I4		2,86 45,77 0,46 I,56	2,28 49,85 0,50 I,43 2,42	5,93 6,74 4,61 0,05
20°C	2,65 69,84 0,69 1,37 2,96	2,70 55,37 0,55 I,44 8,00	2,87 49,01 0,49 1,70 3,10	2,45	6,35 7,20 6,35 0,06
*0°C	2,70 3,50 113,95 1,14 1,44	2,82 67,97 0,68 1,96 3,15	2,67 61,99 0,62 1,53	2,43 78,61 C,77 I,63 2,69	6,30 6,85 0,07
50°C	2,62 3,86 I39,17 I,39 I,76	2,70 99,08 0,99 2,12 3,20	2,67 76,32 0,76 2,13 3,42	2,34 2,79 III,27 I,II 2,IO	6,26 m,19 0,11 7,20
70 ⁹ C	2,62 3,75 167,68 1,68 1,76	2,82 114,29 1,14 2,40	2,82 3,31 89,50 0,50 2,08	2,26 2,64 122,07 1,22 2,22	

*Translator's Note: Commas in the numbers represent decimal points.

The differences and the properties of the reagents become most apparent with an increased temperature, i.e., their differing chemical nature. Based on their action on biotite, they can be arranged as follows: $H_2C_2O_4 > H_2SO_4 > \text{ulmic acid} > \text{fulvic}$ acid > H_2O . The percentile decomposition of biotite by acids is approximately 10 - 15 times greater than by water.

Humic acids, in terms of their action on biotite, approximate inorganic sulfuric acid; oxalic acid exceeds it. Neutralization of natural organic acids takes place up to higher values of pH (Table 1).

The differing ratio of organic acids to iron and aluminum /137 is more pronounced at higher temperatures. Thus, humic acids change into solutions a larger amount of iron than of aluminum (in percent of the initial content in the mineral). Oxalic acid is practically the same in terms of iron and aluminum, i.e., humic acids have a greater affinity for iron, and oxalic acids have the same affinity for aluminum and iron.

Increased contents of titanium (4 — 5 times greater than in solutions of sulfuric acid) can be observed in solutions of organic acids. The reason for the unequal ratio of organic acids to iron, aluminum, and titanium must be found in the differing properties of the acids. The similar contents of carbon in the solutions before and after experiments point to the lack of precipitation of organic matter.

Decomposition of nepheline. It may be seen from the data in Table 2 that nepheline is decomposed by acids to a much greater extent than biotite, but with water, on the other hand, to a much lesser extent than biotite. The percent of the total decomposition of nepheline by acids barely changes with a

TABLE 2*

INFLUENCE OF TEMPERATURE ON THE TOTAL DECOMPOSITION OF NEPHELINE (mg/l in %)

Temper- ature	:	05 and oxali 1. mg/1 % Side in in		(pH pH in	of podzol mg/1 / s. i	layer)		and H ₂ SO ₄ mg/1 %Sio	2 ¹⁴¹ 2 ⁾ 3 solution	pH ir	
+5°C	2,60 5,25	200,58 2,01	I,44	2,80 4,26	172,25 I,72	2,22	2,30 4,05	219,39 2,19	I,54	5,97 5,98	0,810,008
+10°C	2,62 5,05	210,58 2,11	1,52	2,86 4,25	148,47 I,48	2,15	2,36 3,99	207,66 2,08	1,58	5,93 6,22	0,82 0,008
+20°C	2,65 5,48	185,13 1,85	1,63	2,87 4,32	162,23 I,62	2,25	2,45 4,0I	191,41 1,91	1,97	6,20 6,67	1,73 0,017
+40°C	2,66 5,38	197,57 1,98	1,69	2,87 4,42	177,65 1,78	2,47	2,43 4,06	208,27 2,08	2,04	6,32 6,57	1,37 0,013
-60°C	2,82 5,70	202,07 2,02	1,65	2,87 4,70	195,25 I,95	2,88	2,34 3,65	216,79 2,17	2,23	6,26 8,IO	5,97 0,060
4,0°5	2,62 5,85	206,94 2,07	1,68	2,80 4,35	188,19 1,89	3 ,00	2,26 3,40	224,08 2,24	2,44	-	- -
	S10 ₂ :	M ₂ 0 ₃ in ini	tial nephe	eline	2,27						

^{*}Translator's Note: Commas in the numbers represent decimal points.

temperature increase and comprises about 2% on the average. Water begins to decompose it noticeably only above 40° C.

For the decomposition of nepheline, the pH of the solutions after experiments for different acids is located between 4 — 6. This is naturally reflected in the behavior of elements such as aluminum and silicic acid (the phenomena of the hydrolysis of compounds of aluminum and polymerization of silicic acid arise). The content of alkalis and partially of silicic acid increases in solutions of sulfuric acid and fulvic acids with a temperature increase, whereas the aluminum content gradually decreases or remains constant. In solutions of oxalic acid, the content of all the elements barely changes.

With an increase of temperature, in fulvic acid extracts from nepheline, the content of organic carbon decreases by 10-30% from the original value, and the residue of undecomposed nepheline takes on a cinnamon color. The behavior of the ele- $\frac{138}{138}$ ments and carbon in the solutions points to the precipitation of nepheline decomposition products. This is also confirmed by the turbidity of fulvic acid solutions and the appearance of residues in the oxalic acid solutions after a few days.

Sharp differences in the action of the acids on nepheline are not observed. In solutions of fulvic acids, there is a somewhat reduced content of aluminum (the average content for all temperatures is approximately $50 \text{ mg/} t \text{ Al}_2\text{O}_3$) as compared with sulfuric and oxalic acids (about $70 - 80 \text{ mg/} t \text{ Al}_2\text{O}_3$). The acids decompose nepheline at 45° C 250 times more vigorously than water, and at 460° C 33 times more vigorously.

Water decomposes biotite and nepheline in different ways. The intra-salt distribution of alkalis in biotite makes them very suitable for leaching by water even at low temperatures. Therefore, an increase in them has little effect on the quantitative amount of these elements passing into solution. Up to $\pm 40^{\circ}$ C, sodium and potassium, as well as silicic acid, may be extracted from nepheline in small amounts (0.3 — 0.4 mg/t). Their content sharply increases when significant amounts of silicic acid enter the solution at temperatures above 50° C. This coincides with the characteristics of alkali decomposition in the structure of nepheline and the change in the water properties at temperatures above 50° C.

In conclusion, we should point out the difference between the influence of temperature on the decomposition of biotite and nepheline. Under the experimental conditions, where the decomposition of biotite is performed under acid conditions (pH = 4.0) with predominance of the decomposition process, the temperature increase contributes to all components of the mineral passing into solution. In experiments with nepheline, where pH of the solutions is greater than 4.0 even at low temperatures, due to the high decomposition rate, an increase in temperature does not change the percent of mineral decomposition, but leads to differences between the forward and reverse processes (decomposition and precipitation).

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